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In re Applicant:

Franklin E. Parks

Filed: August 13, 2001

Serial No.: 09/928,764

For: Polyurethane Films and Dispersions  
For the Preparation Thereof

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Group Art Unit: 1711

Examiner: Rabon A. Sergent

Attorney Docket No.: 44446 US  
(019131/02700)

**DECLARATION OF BEDRI ERDEM, Ph.D. UNDER 37 C.F.R. § 1.132**

I, Bedri Erdem, do hereby declare and state:

1. I am over the age of 18.
2. I earned a B.S. degree (1989) and M.S. degree (1994) in Chemistry from Karadeniz Technical University in Trabzon, Turkey, and a Ph.D. (2000) in Polymer Science & Engineering from Lehigh University.
3. For two and one half years, I have been employed by The Dow Chemical Company. Since that time, I have worked in research and development relating to polyurethane dispersions.
4. I have read and understand the specification of U.S. patent application serial no. 09/928,764, filed on August 13, 2001, which is directed to novel polyurethane films and a method of making the same and an aqueous polyurethane dispersion useful for preparing the polyurethane film. The dispersions are made by first preparing the non-ionic prepolymer. Water and an anionic surfactant are then added to the prepolymer, thereby rendering the polyurethane

dispersion. The polyurethane dispersions produced by the claimed process exhibit properties similar to natural rubber latexes without the inclusion of dermal irritants and solvents.

The process claimed in U.S. patent application serial no. 09/928,764 renders unexpected results as compared to the process of adding water to the prepolymer prior to the addition of an anionic surfactant. This is illustrated in the experiments reported below which were conducted under my direction and control.

5. Preparation of Polyurethane Prepolymer. The prepolymer was prepared by blending aromatic diisocyanate, 4,4'-methylene diisocyanate (MDI) (Isonate 125M<sup>®</sup>), and polyether polyol mixtures (Voranol 9287<sup>®</sup>, Voranol P-425) in a 32 oz glass bottle (wt. ratios provided in Table 1). The blend of polyols were warmed up in an oven (60 °C) for 10 minutes and added to MDI in a dropwise fashion over a 10 minute period while stirring with a mixer (~60 rpm). Given that MDI is a solid at room temperature, it was melted in the oven (55 °C) before use. One drop of benzoyl chloride (~ 50 ppm) per 800 g of prepolymer was added to the reaction mixture. The mixture was stirred under a nitrogen pad (30 rpm using a hand mixer) before it was placed in oven at 80 °C for 30 minutes. The prepolymer was removed from the oven and mixed using a hand mixer (~60 rpm) and replaced in the oven for 3.5 hours at 80 °C. Subsequently, the vessel and contents were allowed to cool to ambient temperature. Table 1 below shows the composition of the prepolymer prepared:

Table 1

Sample No	MDI (wt%)	Polyol	
		Voranol 9287* (wt%)	Voranol P425** (wt%)
1	33.3	52	14.7

\*Voranol 9287, a poly propylene oxide-ethylene oxide diol with 12.5 wt % total end capping (6.25 wt% at each end), is a product of The Dow Chemical Company.

\*\*Voranol P425, an all polypropylene oxide diol with a molecular weight of 425, is a product of The Dow Chemical Company.

#### Preparation of Polyurethane Dispersions (PUD):

(A) Surfactant Added during Fabrication of PUD. In Example Nos. 1 and 2, 200 g of prepolymer was placed in a 32-oz glass bottle and a 2.75 inches Cowles blade was inserted into the bottle such that the blade was just covered by the liquid prepolymer. A 4.0 wt% surfactant solution (based on prepolymer) (38 g for LDS-22 and 31.8 for SLS) was diluted with small fraction of dilution deionized water (40 g of total water) and poured onto prepolymer as the mixing was started (3000 rpm). The rest of the water (184 g) was added into mixture slowly dropwise over 4 minutes. The dispersions obtained were transferred in a half-gallon container and occasionally stirred every 10 minutes with a hand mixer and allowed to degas under atmospheric pressure.

In Example Nos. 1A and 2A, 200 g of prepolymer was placed in a 32-oz glass bottle and a 2.75 inches Cowles blade was inserted into prepolymer such that the blade was just covered by the liquid prepolymer. The initial deionized water (196 g) was poured onto the prepolymer as the mixing was started (3000 rpm). The rest of the water (40 g) and surfactant solution (38 g for LDS-22 and 31.8 for SLS) was mixed slowly onto the solution and stirred at 3000 rpm.

The results obtained from these studies are summarized in table 2 below:

Table 2

No.	Prepolymer (g)	Surfactant (LDS-22 <sup>+</sup> , g)	Surfactant (SLS <sup>++</sup> , g)	DI water	Particle size (mm)	
					After 10 min	After 24 days
1	200	38	-	224	491	537
1A <sup>*</sup>	200	38	-	224	1964 <sup>*</sup>	Coagulated
2	200	-	31.2	236	355	596
2A <sup>*</sup>	200	-	31.2	236	1122 <sup>*</sup>	Coagulated

\* Completely coagulated after 15 minutes.

<sup>+</sup> LDS-22: Sodium salt of dodecyl benzene sulfonates (22 wt% active);

<sup>++</sup> SLS: Sodium Lauryl Sulfonate (29 wt% active) Para-chem

<sup>++</sup>Dynamic Light Scattering – Particle Size Measurement (Coulter LS-230 was used for the determination of particle size) 1 drop of sample was added onto 20 g of deionized water. Several drops of the resulting solution introduced into sample chamber after calibration of laser beam was conducted using deionized water.

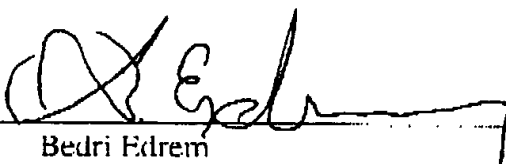
Results and Discussion: The resulting dispersion was immediately characterized in terms of their particle size. In the case where both the SLS and LDS-22 surfactants were added to the prepolymer prior to the addition of water, the resulting dispersions were stable and had low viscosities (<20 cps). These dispersions remained stable for several days (>> 4 weeks) without formation of any aggregates or coagulation despite slight change in their particle sizes. See Exhibit A (wherein the anionic surfactant was SLS) and Exhibit B (where the anionic surfactant was LDS).

However, with the dispersions prepared by the addition of water into the prepolymer prior to the addition of surfactant (both SLS and LDS-22), large chunks of coagulated prepolymer in the solution were observed. These chunks were completely coagulated after 15 minutes of stirring. See Exhibit C (wherein the anionic surfactant was SLS) and Exhibit D (wherein the anionic surfactant was LDS).

I therefore conclude that the method for producing polyurethane dispersions by the addition of anionic surfactant and water to the prepolymer is effective for rendering stable polyurethane dispersions whereas the method of adding water into the prepolymer prior to the addition of an anionic surfactant is an ineffective method for producing polyurethane dispersions. The latter method does not render stable polyurethane dispersions.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and believe are believe to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under 18 U.S.C. § 1001 and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

DATED: 6/27/02

  
Bedri Edrem